

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-268890

(43)Date of publication of application : 29. 09. 2000

(51)Int. Cl.

H01M 14/00

H01L 31/04

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(54) PHOTOELECTRIC TRANSDUCER AND PHOTSENSITIZING PIGMENT FOR
TRANSDUCER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photoelectric transducer of photosensitizing type consisting of solid substance having an excellent photoelectric conversion efficiency capable of suppressing exfoliation of each electrode from an electric charge conveying layer and accomplishing a long lifetime of cell.

SOLUTION: This photoelectric transducer is composed of a semiconductor electrode 3a pigment 4 carried thereby and expressed by ML1L3L4L5 and/or ML22L6L7 and an electric charge conveying layer 5 including a bond with the pigment 4. In the expression for the pigment M is either of ruthenium osmium and iron L1 and L2 are organic ligand unsubstituted or substituted with 1-3 carboxyl radical hydroxyl radical sulfon radical or cyano radicals and at least one of L3-L5 and also of L6-L7 is able to form a bond of M with the electric charge conveying layer by a coupling radical expressed by X-Y where X is either of the hydroxyl radical thiol radical carboxyl radical phosphonic group sulfonic group and amino radical while Y is two-valent aromatic compound of C3-30 substitution or non-substitution.

CLAIMS

[Claim(s)]

[Claim 1] Coloring matter expressed with following ML1L3L4L5 and/or ML2₂L6 L7 which it was supported on a semiconductor electrode and said semiconductor electrode and have been chemically combined with a charge transport layer via a chemical bond group [M is chosen from a ruthenium osmium and iron among a formula and L1 and L2 By an organic ligand of two seats respectively replaced independently by at least one sort of substituents chosen from un-replacing or one two or three carboxyl group hydroxyl a sulfone group and a cyano group or three seats. Among L3-L5 or L6 - L7 respectively at least one. X-Y- (X [however] -- a hydroxyl group a thiol group a carboxyl group and a phosphonic acid group.) It is a substituent chosen from a group which consists of a sulfonic group and an amino group coordinating to the central metal M -- Y -- from divalent substitution or an unsubstituted aromatic-compounds structure of the carbon numbers 3-30 -- becoming -- an optoelectric transducer which is the bond groups expressed and is characterized by having a charge transport layer which has] chemically combined with a charge transport layer via the bond groups.

[Claim 2] ML1L3L4L5 and/or ML2₂L6 L7 [M is chosen from a ruthenium osmium and iron among a formula and L1 and L2 By an organic ligand of two seats respectively replaced independently by at least one sort of substituents chosen from un-replacing or one two or three carboxyl group hydroxyl a sulfone group and a cyano group or three seats. Among L3-L5 or L6 - L7 respectively at least one. X-Y-Z (X [however] -- a hydroxyl group a thiol group a carboxyl group and a phosphonic acid group.) It is a substituent chosen from a group which consists of a sulfonic group and an amino group Photosensitizing pigment for optoelectric transducers which it is coordinating to the central metal M and Y consists of divalent substitution or an unsubstituted aromatic-compounds structure of the carbon numbers 3-30 and is expressed with Z being a reaction group which can form a charge transport layer and a chemical bond].

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optoelectric transducer which is related with a solid optoelectric transducer and

raised the photoelectricity energy conversion efficiency conventionally and prevented exfoliation with a coloring matter support electrode and a charge transport layer.

[0002]

[Description of the Prior Art] As a photosensitization type solar battery as indicated to the proceedings "solid-state dye-sensitized solar cell" of the Osaka University organicity optical engineering research center-sponsored collection "basic physical properties of a semiconductor photocatalyst and application" of the 5th organicity optical engineering research center symposium gist, Polymer is combined with coloring matter; it is considered as a charge transport layer and there are some which generated electricity. Here the following methods are used by making coloring matter and a charge transport layer into the method of joining not but combining. Ruthenium coloring matter (****- 3-(pyrrole-1-ylmethyl) pyridine-NN'-bis(2'-bipyridyl 44'-dicarboxyl acid) ruthenium (II)) is used as coloring matter. Electrolytic polymerization is carried out in the solution containing pyrrole and ClO_4^- and simultaneously with polypyrrole (charge transport layer) composition combination with coloring matter is made. However, this method also has light energy conversion efficiency as low as 1% or less and the actual condition is not having resulted in utilization.

[0003]

[Problem(s) to be Solved by the Invention] In a wet sensitization type solar cell as indicated to the "solid-state dye-sensitized solar cell" of the Osaka University organicity optical engineering research center-sponsored collection "basic physical-properties [of a semiconductor photocatalyst] and application" proceedings of the 5th organicity optical engineering research center symposium gist, It is also one method to carry out the chemical bond of the semiconductor electrode and solid charge transport layer to which coloring matter was made to stick. However, since combination is between coloring matter and a charge transport layer as compared with the time of combination not having an electronic transition since the coloring matter used here has a bad absorption feature and the long wavelength absorption feature is bad in spite of being carried out at high speed. There was a problem that the photoelectricity energy conversion efficiency was decreasing or less [of a wet cell] to 1/10.

[0004] In this invention, the problem of exfoliation with a light energy conversion efficiency fall and coloring matter and a charge transport layer when a charge transport layer which was described above is used as a solid by forming a charge transport layer and a chemical

combination and using coloring matter also with good light absorption characteristics is solved simultaneously.

[0005]

[Means for Solving the Problem] In this invention by a charge transport layer combining coloring matter and a charge transport layer in a solid dye sensitizing type optoelectric transducer. An electric charge which can move per unit time between a coloring matter-charge transport layer increases and light energy conversion efficiency is high and also exfoliation between coloring matter and a charge transport layer can be prevented and an element which can solve a problem looked at by optoelectric transducer using the conventional solid charge transport layer at a stretch is provided.

[0006] Specifically combine firmly a charge transport layer and a coloring matter support electrode with a ligand of coloring matter using a ligand with a basis which can form a charge transport layer and a chemical bond and further by the ligand. In order that the optical absorption nature of coloring matter may long-wavelengthize light energy conversion efficiency can improve by leaps and bounds and junction light energy conversion efficiency and a problem of exfoliation which were problems in a solid charge transport layer until now can be solved simultaneously.

[0007] Although electronic transition of a cell indicated to the above-mentioned collection of the 5th organicity optical engineering research center symposium gists to a charge transport layer was improving rather than a time of using coloring matter without combination there was a problem in light energy conversion efficiency being 1/10 or less [of 1% or less and a wet cell]. As a result of our inquiring in detail with this coloring matter as for a cause of decline in light energy conversion efficiency it turned out that light absorption characteristics are because a fall i.e. absorption is carrying out short wavelength formation rapidly. If absorption of coloring matter falls when a complex is used for coloring matter and coloring matter and a charge transport layer are combined a cause of the fall It thought that it was in a ligand of a side combined with a charge transport layer instead of a ligand of a side which is sticking to a semiconductor electrode and its attention was paid to a ligand of a side combined with a charge transport layer. The kind was changed variously and the characteristic of coloring matter or a cell was evaluated. As a result when the portion itself configured in a central metal like pyridine used a molecule which has a ring structure as a ligand with a charge transport layer and combination it turned out that the long wavelength absorption feature of coloring matter gets

worse remarkably and light energy conversion efficiency falls. on the contrary a functional group (for example a hydroxyl group a thiol group and a carboxyl group.) which carries out a coordinate bond Structure which organic molecules such as the benzene ring have combined with a phosphonic acid group a sulfonic group and an amino acid group A result of a coordination portion and a hydrocarbon portion not having a ring structure and the light absorption characteristics of coloring matter having improved by leaps and bounds and carrying out long wavelength absorption of the molecule which a skeleton of a ligand sees macroscopically and has linear structure with coloring matter used for a ligand was obtained. A result light energy conversion efficiency naturally indicates improvement in wonderful to be as a cell was brought. [0008] In a cell in which coloring matter and a charge transport layer do not have combination a volume change accompanying a phase change when impregnating with a difference and a charge transport layer of a coefficient of thermal expansion between coloring matter-charge transport layers etc. can be considered as a cause by which exfoliation breaks out between coloring matter-charge transport layers. Since it is junction only by Van der Waals force when it does not have combination molecules only adjoin and it cannot approach to sufficient distance for an electron to win popularity at high speed and to be passed. However by having combinations since molecules will be connected and it will be connected with a covalent bond an electronic transition came to be performed at high speed. An aromatic ring or a hydrocarbon portion which a portion configured in a central metal an aromatic ring or a hydrocarbon portion has combined by 1-fold combination as a structure of coloring matter and which had a charge transport layer and combination for the ability to fold can rotate focusing on the 1-fold combination. Therefore it has the flexibility of structure as a ligand and coloring matter and exfoliation by heat stress etc. does not take place.

[0009]

[Embodiment of the Invention] When it becomes an optoelectric transducer the coloring matter (it may be hereafter called sensitizing dye) by this invention combines with a charge transport layer chemically via bond groups and is following $ML_1L_3L_4L_5$ and/or $ML_2L_6L_7$. [M is chosen from a ruthenium osmium and iron among a formula and L1 and L2 By the organic ligand of two seats respectively replaced independently by at least one sort of substituents chosen from un-replacing or one two or three carboxyl group hydroxyl a sulfone group and a cyano group or three seats. Among L3-L5 or L6 - L7 respectively at least one. X-Y- (X

[however] -- a hydroxyl group a thiol group a carboxyl group and a phosphonic acid group.) It is a substituent chosen from the group which consists of a sulfonic group and an amino group coordinating to the central metal M -- Y -- from the divalent substitution or unsubstituted aromatic-compounds structure of the carbon numbers 3-30 -- becoming -- it is the bond groups expressed and is expressed with] chemically combined with the charge transport layer via the bond groups.

[0010] In the coloring matter simple substance which has not joined together as shown in claim 2 respectively of L3-L5 or L6 - L7 at least one. [of a ligand] X-Y-Z (X [however] -- a hydroxyl group a thiol group a carboxyl group and a phosphonic acid group.) It is a substituent chosen from the group which consists of a sulfonic group and an amino group and it is coordinating to the central metal M. Y consists of the divalent substitution or unsubstituted aromatic-compounds structure of the carbon numbers 3-30 and Z has become a reaction group which can carry out a charge transport layer and a chemical bond.

[0011] By having combination with a charge transport layer from a charge transport layer at high speed the coloring matter by such this invention wins popularity and comes to be passed. Combination with a charge transport layer is firm and exfoliation between coloring matter-charge transport layers does not take place easily and light absorption characteristics are good and it is the greatest feature that the effect [conversion efficiency / light energy] wonderfully that it is high happens simultaneously.

[0012] As for sensitizing dye in order to combine with a semiconductor electrode strongly it is preferred to have a functional group which can be adsorbed or combined by the chemical interaction on the surface of a semiconductor electrode. For example it is preferred to have functional groups such as a carboxyl group hydroxyl a sulfone group and a cyano group in a molecule.

[0013] sensitizing dye -- the coloring matter of 6 coordination -- it RuLa₃(ing)RuLb₂(ing) and preferably RuLc₂L₂RuLdL₃OsLa₃ With the coloring matter of 6 OsLb₂OsLc₂L₂OsLdL₃FeLa₃FeLb₂FeLc₂L₂ and FeLdL₂ type coordination. It had a functional group which can have adsorption or combination in a semiconductor electrode as mentioned above could adsorb or combine with the semiconductor electrode and has combined with the charge transport layer via bond groups like X-Y- of a statement further at the claim to a central metal. The ligand of the side which specifically makes the charge transport layer and combination of coloring matter general formula X-Y- (X -- a hydroxyl group a thiol group a carboxyl group and a phosphonic acid group.) It was chosen out of the group which consists of a sulfonic

group and an amino group and has configured in the central metal M and Y is the divalent substitution or unsubstituted aromatic-compounds structure of the carbon numbers 3-30 By the functional group to which the electronic state of coloring matter is changed preferably it is replaced and A more desirable substituent electron-donative in a functional group For example it is important to use the ligand which the coordination portion which can be expressed in writing by $-O-R-N-RCOORCONR_2COR$ (R is an alkyl group) etc. and one-fold aromatic ring portion have combined. Y A phenylene derivative a phenylenevinylene derivative a biphenylene derivative A thienylene derivative etc. are preferred and the structure containing hydroxymethylepoxy groups such as halogenation methyl allyl groups such as a chloromethyl phenyl group and a hydroxy methylphenyl group a thiophene derivative a pyrrole derivative an aniline derivative etc. is good.

[0014] If such coloring matter is used as an adhesive property with a semiconductor electrode a charge transport layer and each improves it can become possible to prevent exfoliation by a thermal excursion etc. etc. and the endurance of a solar cell can be raised. Depending on the ligand portion combined with the charge transport layer this will have the structure where a molecule is soft because between the coordination portion to the central metal of coloring matter and structures with an aromatic ring or conjugate has 1-fold combination and neither decomposition nor secession will take place between the coloring matter-charge transport layers by stress. The light absorption characteristics of the coloring matter using the ligand of such a structure are improving by leaps and bounds and since the charge transfer from a charge transport layer to coloring matter becomes as [perform / charge transfer / at high speed and smoothly] it becomes possible to raise light energy conversion efficiency of them substantially. Coloring matter could have combination with coloring matter and should just be eventually connected with combination with firm above coloring matter and charge transport layers. A desirable optoelectric transducer has coloring matter in which the ligand portion combined with the charge transport layer of coloring matter and the charge transport layer are carrying out conjugate and a charge transport layer by this invention.

[0015] A charge transport layer receives an electron from the counter electrode surface at least and it consists of the carrier supporting material or carrier conductivity material which serves to return the coloring matter which became trivalent by passing coloring matter to divalent. An electron or a hole or ion may be sufficient as the carrier which moves in the inside of a charge transport layer. As for ion the

ionic species in which oxidation reduction is possible are used reversibly. Such materials which constitute a charge transport layer are illiquid and the thing of the gel state or a solid state is used.

[0016] As for a charge transport layer as shown below every material has coloring matter and combination eventually. As bond groups when coloring matter and a charge transport layer have combination Carbon-carbon bonding a carbon-oxygen bond C-N-C-Si-Si-O-etc. are preferred from a point of bond strength for example a methylene group an ether bond a thioether bond an ester bond an amide bond imide bonding a siloxane bond etc. are raised. It is desirable to choose especially bond groups in which a charge transport layer carries out conjugate to a ligand in the case of a hole transportability layer.

[0017] When a career is ion as a material system which constitutes a charge transport layer 1. solid electrolyte materials 2. gel electrolyte material 3. fused salt electrolyte material etc. can be used good.

[0018] 1. As solid electrolyte material the ionic species in which oxidation reduction is possible and the mixture of an ion-conductive high molecular compound are used reversibly. Especially if oxidation reduction is reversibly possible for ionic species will not be limited but. For example the ion (I^-/I^{3-}) of iodine the ion (Se^{2-}/Se_2^{2-}) of selenium ion (Te^{2-}/Te_2^{2-}) of a tellurium ferro cyanogen / FERI cyanide ion $[Fe(CN_6)]^{4-}/[Fe(CN_6)]$ Ionic species such as cyano complexes of metals such as 3^- tungsten and molybdenum $H_3PO_2^-$ and $S_2O_4^{2-}$ are mentioned. As an ion-conductive high molecular compound polar high molecular compound such as for example polyether polyester polyamine and polysulfide are used.

[0019] 2. As a gel electrolyte material the ionic species in which oxidation reduction is possible and the thing ** constituted are used for ** polar organic solvent ** gelling agent and ** reversible target good. ** A polar organic solvent will not be limited especially if the ionic species of ** are dissolved good but it is preferred that it is an aprotic organic solvent. For example ester species such as acetonitrile ethylene carbonate propylene carbonate lactone or the mixture of those can be considered. ** As a gelling agent a polymer gelling agent is used good. For example polymer gelling agent such as polymer which has nitrogen-containing heterocyclic quaternary compound salt structure etc. are used for a cross-linked-poly acrylic resin derivative a cross-linked-poly acrylonitrile derivative a polyalkylene oxide derivative or silicone resin and a side chain. ** As ionic species in which oxidation reduction is possible the same ionic species can be used reversibly as the paragraph of 1. solid electrolyte described.

[0020] 3. What the molten salt electrolysis liquid which the ionic

species in which oxidation reduction is possible dissolved in ordinary temperature type fused salt reversibly was gelling by the gelling agent as a fused salt gel electrolyte material or the ordinary temperature type fused salt in which oxidation reduction is possible gelled by the gelling agent is used. It can be with the ionic species reversibly same as ionic species in which oxidation reduction is possible as the paragraph of 1. solid electrolyte described. As ordinary temperature type fused salt nitrogen-containing heterocyclic quarternary-ammonium-salt compounds such as pyridinium salts and imidazolium salts are used good. The above nitrogen-containing heterocyclic quarternary-ammonium-salt compounds which use as an opposite anion the ionic species reversibly same as fused salt in which oxidation reduction is possible as the paragraph of 1. solid electrolyte described are used. The same polymers gelling agent can be used as a gelling agent as the paragraph of 2. gel electrolyte material described. It is good also considering the high molecular compound which furthermore has nitrogen-containing heterocyclic quarternary-ammonium-salt structure as a side chain as a gelling agent.

[0021] As a solid hole or an electronic transition material the high molecular compound which has the organic low molecular weight compound these holes or electron-transport-property molecular structure of crystallinity or amorphous nature in a side chain or a main chain a conjugate property high molecular compound etc. are used. As a hole or an electron-transport-property compound as what has crystallinity for example electron donor acceptor complexes such as a polycyclic aromatic derivative and tetrathiafulvalene such as various metal-phthalocyanines derivatives perylene tetracarboxylic acid perylene and coronenes and tetracyano quinodimethanes etc. can be mentioned -- as an amorphous material -- for example [0022]

[Formula 1]

It comes out and an aluminium compound diamine various ONISA diazole derivatives etc. which are shown are mentioned. As a high molecular compound which has a hole or electron-transport-property molecular structure in a side chain or a main chain it has the hole or electron-transport-property molecular structure mentioned above in a side chain or a main chain and poly-N-vinylcarbazole is mentioned. As a conjugate property high molecular compound conductivity such as a polypyrrole derivative a polyacetylene derivative a polynaphthene derivative a polythianaphthene derivative poly aniline polyphenylenes polyphenylene

vinylene and polysilane or semiconductor nature polymers are mentioned.

[0023] The transparent substrate used by this invention should just be a transparent material for example glass a polymer film etc. are mentioned.

[0024] A transparent conductive layer is transparent and if an electrode surface is material with conductivity it is [anything] good for example it is tin oxide zinc oxide etc. which doped fluoride indium aluminum etc. are preferred. As long as it is a minute amount of a grade which seldom interrupts light transmission an opaque metal layer for example platinum gold silver aluminum copper etc. may be contained.

[0025] It is [anything] good if it is a conductive high material as a counter-electrode. It does not matter even when it is transparent and opaque. Material is electrochemically stable and its conductive high material is preferred for example it can consider metals such as platinum gold silver copper and aluminum graphite the above-mentioned transparent conductive layer etc.

[0026] The material used as a semiconductor electrode should just be a semiconductor with little optical absorption of a light range. In a metal oxide semiconductor an oxide of a transition metal for example titanium zirconium hafnium strontium zinc indium yttrium lanthanum vanadium niobium tantalum chromium molybdenum oxides of tungsten and these multiple oxides or an oxide mixture is preferred. Perovskites like SrTiO_3 , CaTiO_3 , BaTiO_3 , MgTiO_3 and SrNb_2O_6 these multiple oxides or an oxide mixture GaN etc. can be used good.

[0027] A method of producing a semiconductor electrode applies on a substrate a paste which distributed particles of semiconductor electrode material in a solvent. Gaseous phase methods such as the applying method for drying and calcinating a sol gel process and a CVD method which use an alkoxide for a raw material and make a dipping spin coat etc. it and weld sputter anode oxidation method a method of producing an oxide by a solvent interface etc. can be considered.

[0028] In order to adsorb more sensitizing dye the one of a semiconductor electrode where surface area is larger is preferred a roughness factor (Rf: thing [as opposed to / thing / an unit area of a substrate] of surface area of an oxide semiconductor which was measured by gas adsorption and a surface area measuring instrument by mercury pressure ON etc.) -- at least 20 or more -- I hope preferably that there are 1000 or more still more preferably 100 or more. In order to enlarge surface area or in order to change a surface state and to enable it to adsorb more coloring matter when producing a thin film a mold may be used or etching acid alkali treatment etc. may be performed after thin film production. At the time of thin film production add organic polymer beads

etc. it is made to disperse in the case of thin film heat treatment and porous structure may be produced.

[0029] Although it is preferred that it is a crystal as for a semiconductor material even when it is amorphous in part it does not matter even when it is altogether amorphous. There may be an oxygen deficiency.

[0030] In order that a transparent electrode here or a semiconductor electrode may not reduce light volume which reaches coloring matter they have the character which penetrates light of a visible light wavelength area and are what is penetrated not less than 70% more preferably 50% at least 30% about 300 to 800-nm light.

[0031] A cell is preferably producible as follows. A transparent electric conductor layer is provided in a transparent substrate by weld slag CVD etc. and the above-mentioned semiconductor electrode is produced on it. Although any above-mentioned method may be sufficient as a manufacturing method electric conductivity of a semiconductor electrode is high and it is preferred to have bolus body structure with large surface area. Although the semiconductor electrode surface is made to support coloring matter it is preferred to evaporate excess water to some extent in that case. For a certain reason that to which decomposition of coloring matter takes place with moisture is [a semiconductor electrode board] also good to carry out heat treatment etc. before coloring matter adsorption and to reduce a moisture content in an electrode. How to perform simultaneously combination with production and coloring matter of a charge transport layer and a charge transport layer for a charge transport layer by electrolytic polymerization etc. after adsorption to a semiconductor electrode of coloring matter and a method of combination with coloring matter and a charge transport layer make ** coloring matter stick to a semiconductor electrode ** After making coloring matter stick to a semiconductor electrode and applying charge transport layer material how to make react with light or heat and combine a method of combining with ** coloring matter a molecule which constitutes a charge transport layer beforehand and making coloring matter with the charge transport nature child stick to a semiconductor electrode etc. can be considered.

[0032] ** A time of using conjugate property polymers for a charge transport layer as a method etc. can be considered. Add a reaction group to a ligand of a side first combined with a charge transport layer of coloring matter the reaction group and a monomer of a substance to use as polymers are made to react and coloring matter in which a monomer is given to the point of a ligand is produced. Coloring matter is made to

stick to the semiconductor electrode surface by dissolving coloring matter with a monomer which was made such and produced in an organic solvent immersing a semiconductor electrode in the solution and flowing back preferably. Electrolytic polymerization of this coloring matter support semiconductor electrode is dipped and carried out into a solution which melted a monomer and a supporting electrolyte of a charge transporting material to an organic solvent.

[0033]** Make coloring matter in which a reaction group was added to a ligand of a side combined with a charge transport layer as a method stick to a semiconductor electrode. A semiconductor electrode may be immersed in an organic solvent which dissolved coloring matter as an adsorption method and it may flow back preferably. Thus on a produced coloring matter support semiconductor electrode a charge transporting material (if required catalyst of a radical generator etc.) which dissolved in a solid state or a solution is applied and it is made to react or gel by heat or light after desiccation.

[0034]** Produce coloring matter which is combined with a charge transport nature child who shows electrical conduction and make such coloring matter adsorb on a semiconductor electrode in a method. An adsorption method dissolves coloring matter in an organic solvent etc. and is made to adsorb by making a semiconductor electrode immersed into the solution. Under the present circumstances it may flow back.

[0035] A cell is formed by providing an electrode in a coloring matter support electrode with a charge transport layer and combination which were produced as mentioned above.

[0036] Since a loss will become large while passing along a charge transport layer if distance between two electrodes is large when a cell is used if electrodes do not contact the smaller possible one of inter electrode distance is good.

[0037] What is necessary is just to measure a short-circuit current in order to know electron transfer efficiency between coloring matter and a charge transport layer. An electron will flow even through a semiconductor electrode from coloring matter efficiently so that a current value is large. An initial value was compared with a value after prolonged use for this measured value and a desquamative state was judged. It will be thought that it has exfoliated if it seems that it is falling. Light energy conversion efficiency can be easily drawn with a parameter in a formula of the following measured when it irradiated with sunlight (AM1.5).

As for short circuit current density and $V_{oc} \eta_{global} = (i_{ph} \times V_{oc} \times ff) / I_s \eta_{global}$ is [light energy conversion efficiency and i_{ph} / a fill factor and I_s of

open circuit voltage and ff] the intensity of irradiation light.

[0038]

[Example] Although an embodiment of the invention is described below this invention is not limited to this example.

[0039] [Example 1]

1) After adding 21 ml of nitric acid to 5 g of production titanium dioxide ultrafine particles (mean particle diameter of 14 nanometers anatase) of the titanium dioxide layer and fully agitating 3.5 g of polyethylene glycols were added and agitated and the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visually among the air at 440 °C it calcinated for 45 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 °C for 2 hours [0040]

[Formula 2]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposure in the 0.15M isothianaphthene containing 0.1M LiClO₄ and acetonitrile fluid with constant potential

(vs. Ag/Ag⁺) photoelectrical depolymerization of the thianaphthene was carried out and the polythianaphthene layer was formed. Under the present circumstances it was checked that the coloring matter support titanium dioxide thin film had been thoroughly covered with the polythianaphthene layer. The thickness of the polythianaphthene single layer could be 10 microns.

4) Sealing resin is applied to the surroundings of the coloring matter support titanium dioxide thin film produced by the production 3 of the cell and the titanium oxide membrane of the substrate of polyisothianaphthene. The glass substrate which has the tin-oxide electric conduction thin film which doped fluoride was stuck by pressure by hot

pressingsealing resin was solidifiedand the cell of this invention was produced.

5) It took out in the cell produced by the evaluation 4 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0041][Example 2]

1) Clean ultrasonically in ethanol the glass substrate in which the conductor layer of the tin oxide which carried out the production fluoride dope in CVD of a barium titanate layer is providedand use it as a substrate. A raw material is barium. Using beta-diketonate bis(dipivaloyl meta-NATO)barium and titanium isopropoxideit was made to evaporate at 200 ** and 60 **respectivelyand membrane formation was performed for 4 hours by the substrate temperature of 600 **the total pressure of 10 torrsand 2 torrs of oxygen pressure.

2) Adsorption to barium titanate of coloring matter[0042]

[Formula 3]

It comes out30 mg of shown coloring matter is dissolved into the ethanol which carried out dehydrating treatmentand the semiconductor electrode board produced by 1 is made immersed into the solution for 5 hours.

After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support titanium dioxide thin film was prepared.

The joint iodine tetrabutylammonium salt of a charge transport layer and coloring matter 3) 10 mgAs 5 mg and a radical

generatorazobisuisobutironitoriru is dissolved in 2 mg70 mg of poly (ethylene glycol) dimethacrylate (Mw=600) is dissolved in 1-ml THFand an iodine is applied to the substrate with a semiconductor electrode produced by 2and is dried with a dryer.

4) The bead of 10-micron polydivinylbenzene was uniformly bound as a spacer on the coloring matter support titanium dioxide thin film board produced by the production 2 of the cellthe glass substrate in which the tin oxide thin film of the fluoride dope was provided was piled upit left the electrolyte injected holeand the circumference was closed with the epoxy resin. From an injected hole [Iodination tetrapropylammonium] = 0.5M[Potassium iodide] = 0.02M[I₂] The acetonitrile / ethylene

carbonate mixed solution of 0.03M (capacity factors 10/90) = 90 weight sections
 The mixed liquor of poly (ethylene glycol) diacrylate ($M_w=600$) 8.5 weight section
 TORIKACHIRORU pro pantry acrylate 0.5 weight section and azobisiso CHIRONI tolyl (azobisisobutironitoriru) 1 weight section was poured in. The injected hole was sealed with the epoxy resin after pouring. After sealing it heated for 10 hours and 60 ** of cells of this invention were produced.

5) It took out in the cell produced by the evaluation 4 of the cell the electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0043] [Example 3]

1) After adding 25 ml of nitric acid to 8 g of production strontium titanate (mean particle diameter of 50 nanometers) of the strontium titanate layer and fully agitating 4 g of polyethylene glycols were added and agitated and the dispersion liquid of strontium titanate were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visually among the air at 500 ** it calcinated for 45 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the strontium titanate of coloring matter at 120 ** for 2 hours [0044]

[Formula 4]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown sensitizing dye into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

3) Combination with a charge transport layer and coloring matter and production of a cell [1-methyl-3-ethyl-imidazolium iodide] = 0.5M [I_2] = the 1-methyl-3-ethyl-imidazolium of 0.05M -- doria -- a rate solution 90 weight sections Poly (ethylene glycol) diacrylate ($M_w=600$) 8.5 weight section The mixed liquor of trimethylolpropane triacrylate 0.5 weight

section and azobisisobutyronitrile 1 weight section. It applied to the substrate produced by 2) the glass substrate which wound the spacer uniformly and provided the tin oxide conductive layer which carried out the fluoride dope was piled up the circumference was closed with the epoxy resin and the hot press was carried out at 100 °C for 30 minutes. 4) It took out in the cell produced by the evaluation 4 of the cell the electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0045] [Example 4]

1) Prepare 29 g of production ** titanium tetraisopropoxide of a titanium dioxide layer 19 g of drying ethanol and 18 g of ** drying ethanol the pure water 1.8 g and two kinds of solutions of 35% HCl solution 3 g ** add every to ** agitate a little ** to it and produce sol. Carry out the spin coat of the prepared sol and irradiate with ultraviolet rays desiccation and after that and it is made to crystallize on the polymethylpentene board which provided the ITO film and is considered as titanium oxide membrane.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 °C for 2 hours [0046]

[Formula 5]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown sensitizing dye into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

3) On the coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter 20 ml of acetonitrile 10 mg of methyl methacrylate 7 mg of iodine tetrabutylammonium salts and optical radical generator (0.5 mg of trimethylolpropane triacrylate 1 mg of methylbenzo IRUFO mates) mixed liquor are applied and it is made to dry with a dryer. The bead of 10-micron divinylbenzene is uniformly bound as a spacer on it in piles with the bottom mercury-vapor lamp of argon gas atmosphere the optical

exposure was carried out and photo-curing of the polymethylpentene board which provided the ITO film was carried out.

4) It took out in the cell produced by the evaluation 3 of the cell the electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0047] [Example 5]

1) After adding 18 ml of nitric acid to 3 g of production niobium pentoxide ultrafine particles (mean particle diameter of 70 nanometers) of the niobium pentoxide layer and fully agitating 3.5 g of polyethylene glycols were added and agitated and the dispersion liquid of niobium pentoxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visually among the air at 600 °C it calcinated for 45 minutes and cooled to the room temperature.

2) After reheating among the air the niobium pentoxide layer produced by the adsorption 1 to niobium pentoxide of coloring matter at 120 °C for 2 hours [0048]

[Formula 6]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown coloring matter into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support niobium pentoxide thin film was prepared.

3) Combination with a charge transport layer and coloring matter [0049]
[Formula 7]

It comes out and 10 mg of hole conductors and azobisisobutyronitrile 1 mg which is shown are dissolved in 30 ml of acetonitrile it applies to the coloring matter support electrode produced by 2 it is dried the glass substrate in which the tin oxide conducting film which carried out the fluoride dope was provided is piled up and a hot press is carried out at 100 °C for 1 hour.

4) It took out in the cell produced by the evaluation 3 of the cell the electrode was attached and the light energy conversion efficiency which irradiated with sunlight was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0050] [Example 6]

1) After adding 21 ml of nitric acid to 5 g of production titanium dioxide ultrafine particles (mean particle diameter of 14 nanometers anatase) of the titanium dioxide layer and fully agitating 3.5 g of polyethylene glycols were added and agitated and the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visually among the air at 460 °C it calcinated for 40 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 °C for 2 hours [0051]

[Formula 8]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposure within isoindole of 0.15M containing 0.1M LiClO₄ and acetonitrile fluid with constant potential (vs. Ag/Ag⁺) photoelectrical depolymerization of the isoindole was carried out and the poly isoindole layer was formed. Under the present circumstances it was checked that the titanium dioxide layer had been thoroughly covered with the poly isoindole layer. The thickness of the poly isoindole single layer could be 10 microns.

4) Sealing resin was applied to the surroundings of the production titanium oxide membrane of a cell the glass substrate which has the tin-oxide electric conduction thin film which doped fluoride was set it was

stuck by pressure by hot pressing and sealing resin was solidified.

5) It took out in the cell produced by the evaluation 4 of the cell the electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0052][Example 7]

1) After adding 24 ml of nitric acid to 6 g of production strontium titanate ultrafine particles (mean particle diameter of 100 nanometers) of the strontium titanate layer and fully agitating 3.5 g of polyethylene glycols were added and agitated and the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visually among the air at 500 °C it calcinated for 40 minutes and cooled to the room temperature.

2) After reheating among the air the strontium titanate layer produced by the adsorption 1 to the strontium titanate of coloring matter at 120 °C for 2 hours [0053]

[Formula 9]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support strontium titanate thin film was prepared.

3) Combination with a charge transport layer and coloring matter [0054]

[Formula 10]

Come out and 10 mg of hole conductors and BTTB 1 mg which is shown are dissolved in 3 ml of acetonitrile. It applies to the coloring matter support electrode produced by 2) it is dried the glass substrate which wound a 10-micron spacer and in which the tin oxide conducting film which carried out the fluoride dope was provided is piled up and a hotpress is carried out for 5 minutes at 200 °C.

4) It took out in the cell produced by the evaluation 3 of the cell the

electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0055][Example 8]

1) Prepare 29 g of production ** titanium tetraisopropoxide of a titanium dioxide layer 19 g of drying ethanol and 18 g of ** drying ethanol the pure water 1.8 g and two kinds of solutions of 35% HCl solution 3 g ** add every to ** agitate a little ** to it and produce sol. The spin coat of the sol adjusted on the glass substrate which provided the tin oxide which carried out the fluoride dope is carried out heat treatment is carried out at 600 ** desiccation and after that for 30 minutes and it is considered as titanium oxide membrane.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 ** for 2 hours [0056]

[Formula 11]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposure Within the 0.15M isothianaphthene containing 0.1M LiClO₄ and acetonitrile fluid with constant potential (vs. Ag/Ag⁺) photoelectrical depolymerization of the thianaphthene was carried out and the polythianaphthene layer was formed. Under the present circumstances it checked that the titanium dioxide layer was thoroughly covered with polyisothianaphthene. The thickness of the polyisothianaphthene single layer could be 10 microns.

4) Sealing resin is applied around titanium oxide membrane on the coloring matter support titanium dioxide thin film produced by the production 3 of the cell and the substrate of polythianaphthene After setting the glass substrate which has the tin-oxide electric conduction thin film which doped fluoride and being stuck by pressure by hot

pressing the weight was put and sealing resin was solidified every 10 hours.

5) It took out in the cell produced by the evaluation 4 of the cell the electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0057] [Example 9]

1) 0.01 mol of production ** metal barium and 40 mol of isopropanols of a barium titanate layer 0.03 mol of ** pure water 0.7 mol of acetic acid 30 mol of isopropanols ** Three kinds of solutions of 0.01 mol of titanium isopropoxide and 35 mol of isopropanol ** are prepared it adds every to ** and agitate a little ** to it next add 2000 mol of acetylacetone sagitate in 80 ** nitrogen for 2 hours and consider it as a transparent solution. ** is added in the solution and sol is produced. Carry out the spin coat of the sol adjusted on the polymethylpentene board which provided the ITO film and irradiate with ultraviolet rays desiccation and after that and it is made to crystallize and is considered as a barium titanate film.

2) After reheating among the air the barium titanate layer produced by the adsorption 1 in the barium titanate layer of coloring matter at 120 ** for 2 hours [0058]

[Formula 12]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown sensitizing dye into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support barium titanate thin film was prepared.

3) Combination with a charge transport layer and coloring matter [0059]
[Formula 13]

It comes out and 10 mg of hole conductors and azobisisobutyronitrile 1 mg which is shown are dissolved in 1 ml of acetonitrile it applies to the coloring matter support electrode produced by 2 it is dried the glass substrate in which the tin oxide conducting

film which carried out the fluoride dope was provided is piled up and a hot press is carried out at 100 °C for 1 hour.

4) It took out in the cell produced by the evaluation 3 of the cell the electrode was attached and the light energy conversion efficiency which irradiated with sunlight was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0060] [Example 10]

1) After adding 21 ml of nitric acid to 5 g of production titanium oxide ultrafine particles (mean particle diameter of 14 nanometers anatase) of the titanium dioxide layer and fully agitating 3.5 g of polyethylene glycols were added and agitated and the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visually among the air at 460 °C it calcinated for 40 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 °C for 2 hours [0061]

[Formula 14]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposure within isoindole of 0.15M containing 0.1M LiClO₄ and acetonitrile fluid with constant potential (vs. Ag/Ag⁺) photoelectrical depolymerization of the isoindole was carried out and the poly isoindole layer was formed. Under the present circumstances the titanium dioxide layer checked that it had been thoroughly covered with the poly isoindole layer. The thickness of the poly isoindole single layer was 10 microns.

4) Sealing resin was applied to the surroundings of the production

titanium oxide membrane of a cell the glass substrate which has the tin-oxide electric conduction thin film which doped fluoride was set it was stuck by pressure by hot pressing the weight was put and sealing resin was solidified every 10 hours.

5) It took out in the cell produced by the evaluation 4 of the cell the electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0062] [Comparative examples 1-10]

1) each production of a semiconductor electrode layer -- as for the comparative examples 3-10 as well as [the comparative example 2] Example 2 the comparative example 1 produced the substrate with a semiconductor electrode respectively like Examples 3-10 like the method of producing Example 1.

2) 0.001 mol of sensitizing dye shown by adsorption following (a) - (j) to the semiconductor electrode of coloring matter was dissolved into 100 ml of ethanol solutions which carried out dehydrating treatment. After reheating among the air the semiconductor electrode layer produced by 1) at 120 °C for 2 hours the semiconductor electrode was immersed in the coloring matter solution for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and coloring matter support semiconductor membrane was prepared.

[0063] In the comparative example 1 the compound which shows by (h) according to (g) and the comparative example 8 is shown by (i) according to the comparative example 9 and is shown [the comparative example 10] by (j) according to (e) and the comparative example 6 at (f) and the comparative example 7 was used by (d) and the comparative example 5 by (c) and the comparative example 4 according to (a) and the comparative example 2 at (b) and the comparative example 3.

[0064]

[Formula 15]

[0065]

[Formula 16]

[0066]

[Formula 17]

3) To the coloring matter support titanium dioxide thin film produced by being impregnated of a charge transport layer and the production 2 of the cell. At the comparative example 1 it is 1 millimol ***** about the charge transport layer which consists of a compound of (**) and comparative example (**) by (o) and the comparative example 9 by (n) and the comparative example 8 according to (l) and the comparative example 6 in (k) and the comparative example 5 at (m) and the comparative example 7. The charge transport layer of the comparative examples 2-4 is the respectively same substance as the substance of Examples 2-4 and its manufacturing method is also the same.

[0067]

[Formula 18]

[0068]

[Formula 19]

A hotpress is carried out after pulling to a vacuum together with a coloring matter support electrode as a charge transport layer is inserted the same substrate with an electrode of a substrate as the time of producing a semiconductor electrode respectively. Around the back substrate sealing resin is applied and it is made to dry and is considered as a cell.

4) It took out in the cell produced by the evaluation 3 of the cell the electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0069]

[Table 1]

[0070]

[Effect of the Invention] By this invention the solid sensitization type

optoelectric transducer which has photoelectric conversion efficiency equivalent to the sensitization type solar cell of the conventional wet type was obtained fast improve efficiency and exfoliation of an electrode and a charge transport layer were suppressed as compared with the conventional solid sensitization type solar cell and reinforcement of the cell was realized.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram showing the section of the solar cell which is one example of the optoelectric transducer by this invention.

[Description of Notations]

- 1 Transparent substrate
 - 2 Transparent electrode
 - 3 Semiconductor electrode
 - 4 Coloring matter (thing with combination with a charge transport layer)
 - 5 Charge transport layer (thing with combination with coloring matter)
 - 6 Counter-electrode
 - 7 Substrate
-